Control of grain size in sublimation-grown CdTe, and the improvement in performance of devices with systematically increased grain size.

J.D. Major[a*], Y.Y. Proskuryakov[a], K. Durose[a], G. Zoppi[b] and I. Forbes[b]

[a] Department of Physics, Science Laboratories, Durham University, South Road, Durham, DH1 3LE, UK.
[b] Northumbria University, Northumbria Photovoltaic Application Center, Newcastle Upon Tyne NE1 8ST, UK.

* - *corresponding author*

Telephone – 0441913343528

Fax - 0441913345826

Email - j.d.major@durham.ac.uk

Abstract

A method to control the grain size of CdTe thin films deposited by close space sublimation using chamber pressure is demonstrated. Grain diameter is shown to increase in the pressure range 2-200 Torr, following the linear relationship D (μm) = 0.027x P (Torr) + 0.90. A mechanism is proposed to explain the dominance of the 111 preferred orientation in the small-grained, but not the large-grained films. For a series of CdTe/CdS solar cells in which the only variable was grain size, the performance parameters were seen to increase from 0.54% (0.94 μm grains) up to a plateau of 11.3% (≥3.6 μm grains). This corresponds to the point at which the series resistance is no longer dominated by grain boundaries, but by the contacts.

Keywords: Solar; CdTe; Grain size; Sublimation.

1. Introduction

Thin film CdTe used in photovoltaic devices is polycrystalline, and the boundaries between single crystal grains are anticipated to have a significant impact upon the photovoltaic performance of CdTe/CdS solar cells. There is expected to be a high density of defects at the grain boundaries (e.g. dangling bonds, dislocations), and in addition it is possible that impurities and stoichiometric excesses of Te will segregate to the boundary environment. Grain boundaries

in CdTe thin films are generally considered to act as strong electrical recombination centres, due to the introduction of deep energy levels within the band gap resulting from such defects[1]. Grain boundaries may also act as barriers to current transport[2], or to cause significant leakage currents [3]. It is therefore advantageous to device performance to minimise the impact of grain boundaries by maximising the grain size in thin films. Here it is demonstrated that the grain size in sublimation-grown CdTe layers may be controlled by means of the chamber pressure of inert gas. Also it is shown that solar cells made from material having controlled grain size have photovoltaic efficiencies that increase with grain size up to the point at which the grain boundaries cease to dominate the series resistance.

The grain size of CdTe films is known to depend strongly on the deposition temperature[4], with the largest grained films usually being produced by high temperature deposition methods, particularly close space sublimation (CSS). The majority of high efficiency devices reported typically utilise CdTe layers deposited by CSS[4, 5]. Whilst relatively large grain sizes are readily achieved by conventional CSS deposition (3-4μm diameter[4]), there is an upper limit to the substrate temperature (the glass softening temperature) that can be used, and thus to the grain size achievable. Further gains in grain size may be sought by consideration of the nucleation and growth phenomena that lead to the formation of the CdTe thin film. CdTe/CdS thin films have been shown to develop via the Volmer-Weber or “island” growth mechanism[6], where small nuclei form on the surface, before developing to produce grains in the completed film. Films with a larger grain size will therefore be formed when growth conditions are chosen that reduce the likelihood of nuclei forming, thus reducing the density of stable nuclei - and eventually grains - in the completed film. The adatom surface occupancy, ρ, may be approximated by the relation $\rho \approx R\tau_S$, R being the adatom arrival rate at the deposition surface and τ_s the average

lifetime of an adatom the surface[7]. A reduced adatom surface occupancy will decrease the probability of nucleation occurring, owing to the reduced number of adatom surface collisions. Hence by decreasing the arrival rate of species at the surface, surface occupancy - and by extension nucleation density - may be expected to be reduced. In CSS, the adatom arrival rate at the surface may be controlled by altering the rate of sublimation from the source. A simple way to control this is by means of the gas pressure in the sublimation chamber[8], with higher pressures reducing the sublimation rate. It may therefore be expected that the film grain size will be increased for higher chamber pressures. We report a study of the effect of increased nitrogen deposition pressure upon both the grain structure and performance of CSS deposited CdTe/CdS solar cells. This allowed a series of solar cells to be fabricated in which the only variable was grain size, hence allowing the influence of grain size on CdTe solar cells to be quantified directly for the first time.

2. Experimental

A series of solar cell device structures comprising CdTe(~8 μm)/CdS(150 nm)/FTO were grown in which the only variable was the growth conditions used for the CdTe. The transparent conductor was fluorine doped tin oxide (FTO), this being 'TEC8' from Pilkington, cut to 2.5 x 2.5 cm. The CdS was deposited by CSS under 2 Torr of oxygen at source and substrate temperatures of 650ºC and 520ºC respectively. The samples were then transferred to a second CSS chamber in which they were annealed under 3 Torr of hydrogen at a temperature of 400ºC for a period of 2 mins immediately prior to CdTe deposition. CdTe growth took place under various pressures of nitrogen (2, 50, 100 and 200 Torr), at source and substrate temperatures of

600ºC and 460ºC respectively, with the growth time being adjusted to give the same overall thickness of absorber (8μm) in all cases. Since the sublimation rate was reduced by increased pressure, the deposition times were varied in the range 2 min (2 Torr) and 90 min (200 Torr). Following CdTe deposition, a 200 nm thick $CdCl_2$ layer was deposited onto the CdTe back surface by vacuum evaporation, after which the cells were annealed in air at a temperature of 400ºC. The treatment time was optimized for each device (in the range 5-20 min). The cells were then subjected to a 10 s nitric-phosphoric (NP) acid etch, before a matrix (~25) of 2 mm diameter circular gold back contacts were applied by vacuum evaporation.

Physical characterization of the samples was made by SEM (scanning electron microscopy), EDX (energy dispersive x-ray analysis), AFM (atomic force microscopy) and θ - 2θ x-ray diffraction. The photovoltaic performance of the devices was measured from *J* – V curves recorded under approximate AM1.5 conditions at 1000 W/m^2.

3. Results

3.1 Grain size and texture in the CdTe films

Fig.1 shows SEM images taken from the series of CdTe films deposited under pressures of nitrogen in the range 2-200 Torr. Grain diameter values were determined by manual measurement of 100 grains from each SEM image, and the resulting histograms are shown in fig. 2. A graph of the average grain size vs the pressure of nitrogen present during the CdTe growth is shown in fig.3.

Both the images in fig.1 and the statistical data in figs.2 and 3 show very clearly that the grain size increases markedly as the pressure is increased from 2 to 200 Torr. For the lowest deposition pressure used (2 Torr) the average grain diameter was relatively small, 0.94 µm, whilst the maximum diameter observed was 2.01 µm. As the pressure was increased, the grain diameter (D) became larger according to $D = [0.027\,P + 0.90]$µm, where P is the pressure in Torr. Under 200 Torr of nitrogen, the average diameter reached 5.63 µm with a peak of 17.60 µm. It can be seen from the histograms in fig.2 and the error bars in fig.3 (± 1 SD), that the *range* of grain sizes also increased with pressure. Hence for the films with the largest grain average, some relatively small grains (e.g. 1 – 2 µm) persisted.

AFM analysis of the same samples was also performed, with the results being shown in fig.4. All images have the same Z-axis scale, so as to allow direct comparison of the change in the roughness and microstructure of the layers. These images confirm the findings of the SEM measurements, revealing the increased grain size for higher deposition pressures. The roughness of the samples is seen to increase visibly, with those deposited at 2 Torr being smoother (236 nm rms) than those at 200 Torr (965 nm rms).

Fig.5 shows the XRD patterns determined for the CdTe films, whilst table 1 summarises the texture coefficients (C_{hkl})[9] and their spread (as indicated by the standard deviation σ)[10] for each sample. For a randomised sample, $C_{hkl} = 1$ for all peaks, whereas $C_{hkl} > 1$ indicates a preferred orientation. Similarly, for a random sample, the spread of coefficients (and σ) is low, but is high for a textured sample. It can be seen that the sample deposited at the lowest pressure (2 Torr) displays the strongest preferred orientation, with the 111 orientation being prevalent ($C_{111} = 4.58$). This preferred orientation is present for all of the films in the series, but the degree

of texturing decreases with increasing pressure – hence for the film grown under 200 Torr of nitrogen, C_{111} = 1.26 i.e. the film is essentially random with a weak preferred orientation. In order to rule out any influence from systematic compositional differences, EDX analysis of Cd:Te ratio was undertaken for all the films, and a similar result (~1:1) was obtained for each.

Further to the main series of experiments, the possibility to grow even larger grains by increasing the substrate temperature and deposition pressure was investigated. Fig.6 shows a SEM image for a layer deposited at source and substrate temperatures of 650°C and 575°C respectively under a 400 Torr pressure of nitrogen. The average grain diameter was ~16μm, with individual grains having diameters > 45 μm. This demonstrates that considerable grain size gains can be made. However, test devices made from these larger grained samples as part of this work had very poor photovoltaic response. This was considered to be due to the high roughness (~2 μm) and poor physical continuity of the films, there being a high density of pin-holes.

3.2. Performance of devices with systematically controlled grain size

J-V curves were recorded under AM1.5 illumination for all back contact dots from each device (i.e. ~25 *J-V* measurements for each). Typical *J-V* curves for samples with CdTe layers deposited under 2 and 200 Torr nitrogen pressures are shown in fig.7, while the device parameters η, *FF*, V_{oc} and *FF* are plotted as a function of deposition pressure in fig.8.

Figs 7 and 8 indicate a significant increase in performance with pressure up to 100 Torr. The efficiency at 2 Torr has an average of 0.54% (peak of 2.12%), and increases to 11.34% (peak of 13.17%). All device parameters are seen to improve in accordance with this increase, with J_{sc} increasing from 2.17 mA/cm^2 at 2 Torr to 22.80 mA/cm^2 at 100 Torr, whilst V_{oc} and *FF* increased from averages of 0.35 V and 55% to 0.77 V and 77% respectively. However, a plateau

in performance is reached at 100 Torr, there being no further improvement at 200 Torr. This was investigated further by probing the shunt and series resistances of the devices. Under reverse bias, there is little difference between the gradients of the *J-V* curves, implying that there is no major change in the shunt resistance. The series resistance (R_s) for each device was determined from dark *J-V* curves by fitting to the straight line portion of the curve under forward bias, the results being shown in fig. 9. The figure shows that the series resistance is vastly reduced for the larger-grained devices, with a minimum being reached at ~100 Torr, but without further decrease at 200 Torr.

4. Discussion

The results presented in section 3 show that a significant microstructural change in CSS-deposited CdTe films can be achieved by adjusting the pressure of inert gas present during their growth. The observed increase in grain size is presumed to be due to a reduced probability of nucleation occurring under elevated pressure, resulting in a lower nucleation density. This gives a direct method for the control of grain size in CdTe films, with the relationship between grain size and pressure being linear in the range investigated. For a given temperature, it may be expected that the grain size will be dominated by the pressure of inert gas present during growth.

The study of the preferred orientation gives some insight into the mechanisms of grain development. This requires some postulates about the mechanism of the evolution of texture within a film as follows: Postulate 1: that islands nucleate with random orientations, Postulate 2: that the growth of islands in the vertical axis is crystallographically determined i.e. that some orientations grow faster than others. (There is experimental evidence for this see[11, 12]),

Postulate 3: that the fastest-growing orientations ‘outgrow’ the slower ones, and these grain orientations then dominate the orientation of the film. This mechanism was invoked in MOCVD growth of CdTe [13] in order to select substrate orientations that suppressed twinning. If these postulates are accepted, then a difference is expected between the behaviour of films with high and low densities of islands when growth proceeds to a given film thickness (as is the case for these experiments). For the case of high densities, the grains will compete according to Postulate 3, and the preferred orientation will develop in favour of the fastest growing orientation. For the case of low densities of islands, the opportunities for the interaction between grains will be fewer. Growth may be expected to proceed to full thickness without the islands interacting, and hence the original random orientation set is preserved.

The experimental finding of this work, that the preferred orientation is lost upon increasing the grain size, should be compared with that of Ferekides et al [14] in which the 111 orientation *increased* with grain size. This difference in behaviour arises from the fact that in the present work the grain size was influenced by pressure, while in Ferekides’ work, it was controlled by temperature. It may therefore be inferred that it is the growth conditions, rather than the grain size itself, that control the preferred orientation.

The method of grain size control in this work was used as a means to undertake a systematic study of solar cell performance in which the only variable was grain size. It is the appearance of a clear plateau in the improvement of performance parameters that suggests that there is a limiting factor which is revealed at the point when grain phenomena themselves cease to be limiting. This is revealed by the study of series resistances shown in Fig 9: As the grain size is increased, the contribution to R_s from grain boundaries may be expected to decrease also. This

leads to a steady increase in performance. At the performance plateau, R_s ceases to be limited by the grain boundary barriers, and becomes limited by CdTe contact resistance. This conclusion was confirmed by impedance analysis and equivalent circuit modelling of the same series of devices – that work will be reported in detail elsewhere. It is therefore reasonable to expect that further performance gains resulting from an increased grain size may be achieved by means of improved back contacting

5. Conclusion

A method to control the grain size of CdTe thin films deposited by CSS has been demonstrated. SEM and AFM analysis of films grown in the pressure range 2-200 Torr showed grain diameter to increase following the relation, $D = [0.027\ P + 0.90]$ µm. XRD analysis also revealed a loss of preferred 111 orientation for films with a smaller grain size. A mechanism for this was proposed in which i) there is randomly oriented nucleation and ii) the fast-growing orientations dominated by outgrowing the slower ones, but this could only occur when islands were present in high densities and were thus able to interact.

A series of CdTe/CdS devices was grown in which the only intentional variable was grain size.

An increase in efficiency from 0.54% to 11.34% accompanied an increase in grain diameter from 0.94 µm to 5.63 µm. This improved performance was attributed to a reduction in the contribution to series resistance from grain boundary barriers. A plateau in the performance was reached when the series resistance was no longer dominated by grain boundaries, but by the Au/CdTe contact.

6. Acknowledgements

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Figure legends

Figure 1: SEM images of CdTe layers deposited by CSS under different pressures of nitrogen in the range 2 – 200 Torr. The growth times were adjusted to give equivalent layer thicknesses. There is a clear increase in the grain size with increasing pressure.

Figure 2: Grain diameter histograms for CdTe layers deposited under different nitrogen pressures. Each histogram is for measurements from 100 grains from SEM images similar to those shown in fig.1.

Figure 3: Average grain diameter for CdTe layers deposited under different nitrogen pressures. The data was extracted from the histograms in fig. 2, with the error bars being ± 1 SD. The increase in the grain diameter (D) with pressure (P) was fitted to D (μm) = 0.027(± 0.011) x P (Torr) + 0.90(± 0.31).

Figure 4: AFM images of CdTe layers deposited under different pressures of nitrogen, showing the development of roughness as the grain size increases. In all images the field of view is 50 x 50 μm and the Z axis scales are equivalent (6 μm full scale).

Figure 5: θ - 2θ XRD spectra of CdTe/CdS devices with CdTe layers deposited under different nitrogen pressures.

Figure 6: SEM image of CdTe film deposited under 400 Torr of nitrogen and using source and substrate temperatures of 650°C and 575°C. The average grain size in this sample is ~16μm while the largest grain in this image is >45μm.in size. Use of higher pressure and temperatures than for the series in fig. 1 has allowed further increases in grain size.

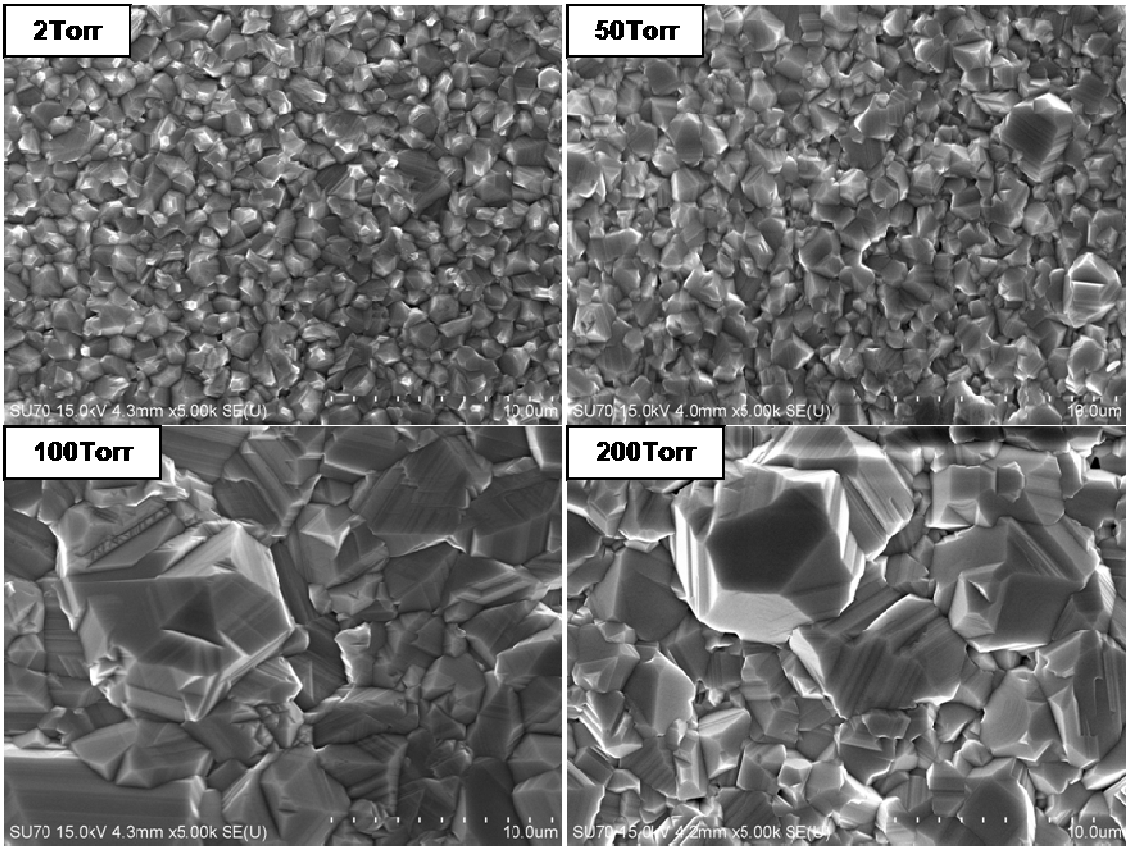
Figure 7: Light *J-V* curves (AM1.5 illumination) for solar cell devices with CdTe layers deposited under 2 Torr and 100 Torr of nitrogen.

Figure 8: Average device performance parameters extracted from *J-V* curves as a function of the background gas pressure present during deposition. Each point represents an average of ~25 contacts with error bars being ±1 S.D. There is a clear increase in all performance parameters with pressure (grain size) up to ~100 Torr, when a plateau is reached. The lines are a guide to the eye.

Figure 9: Series resistance values determined from dark *J-V* curves for cells with CdTe layers deposited under various pressures of nitrogen (the line is a guide to the eye).

Table 1: Values of texture coefficients, C_{hkl}, and degree of preferred orientation deposited under various pressure of nitrogen. As the pressure is increased from 2 to 200 Torr, the degree of 111

preferred orientation declines (C_{111} decreases smoothly from 4.58 to 1.26) and the films become more randomised (the spread of texture coefficient values narrows, and the standard deviation, σ, decreases from 0.78 to 0.24).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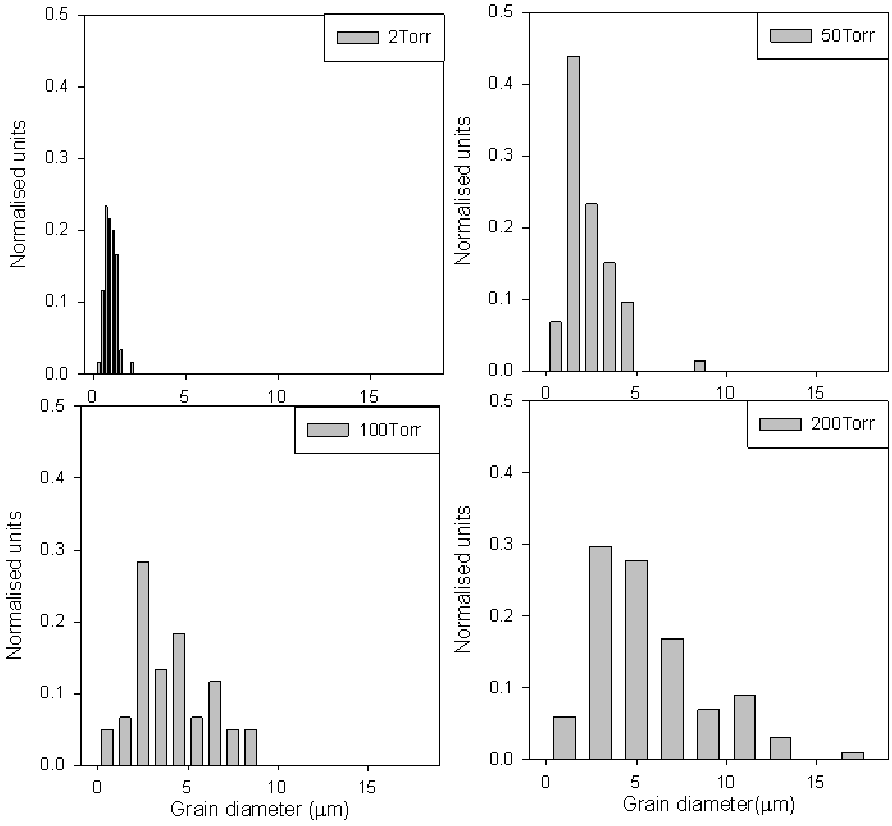
10.0um
200Torr
10.0um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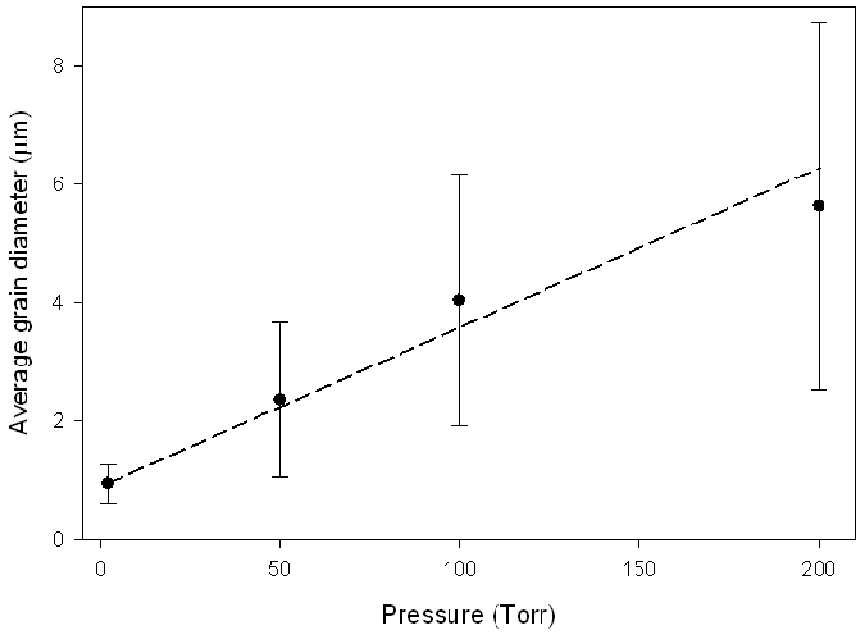
Grain diameter(µm)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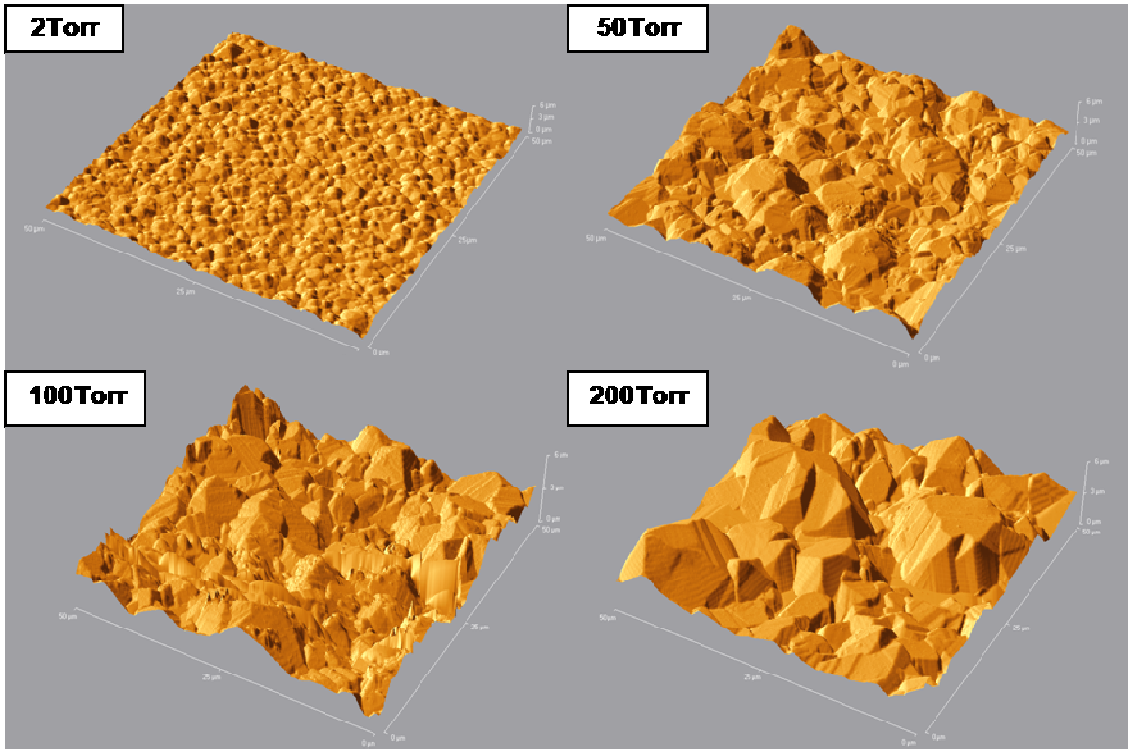
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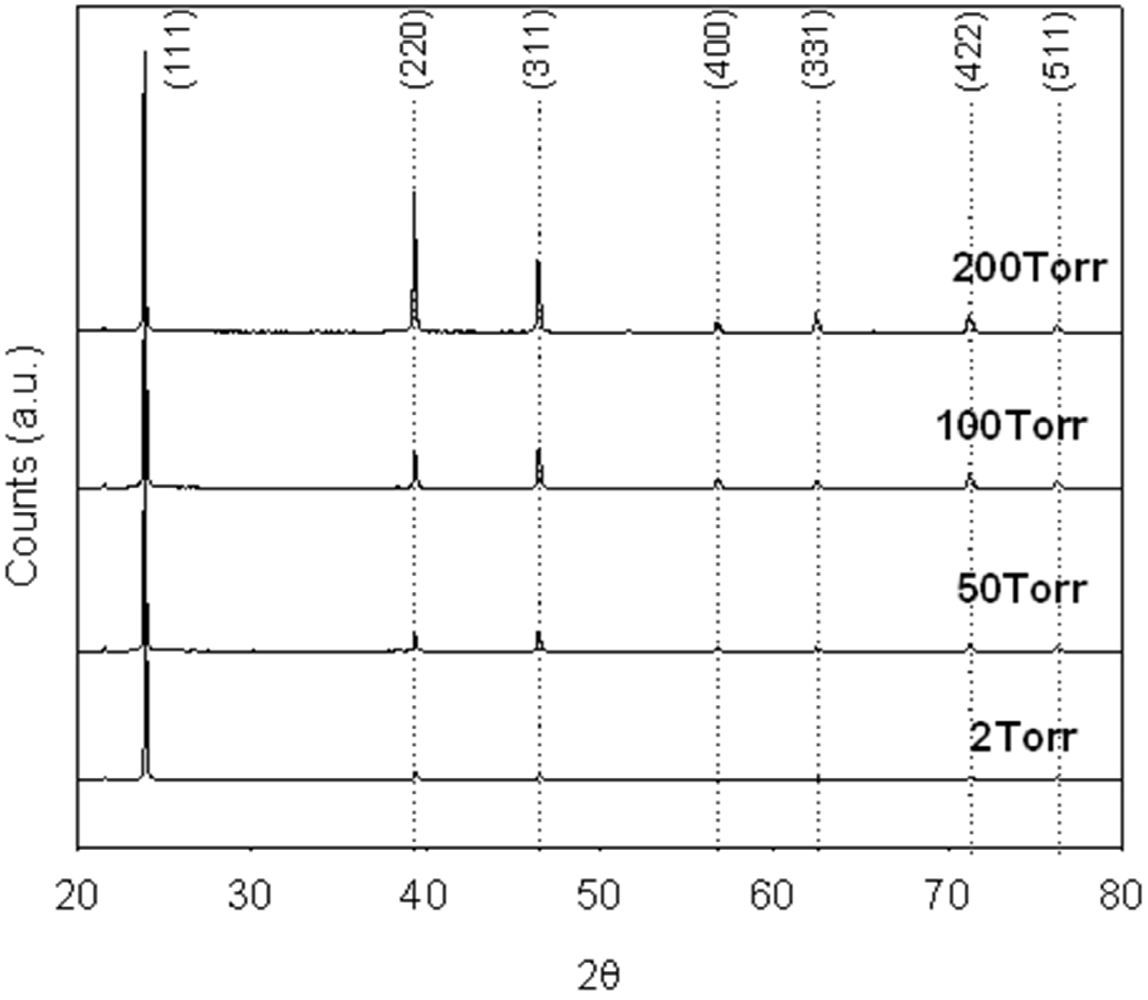
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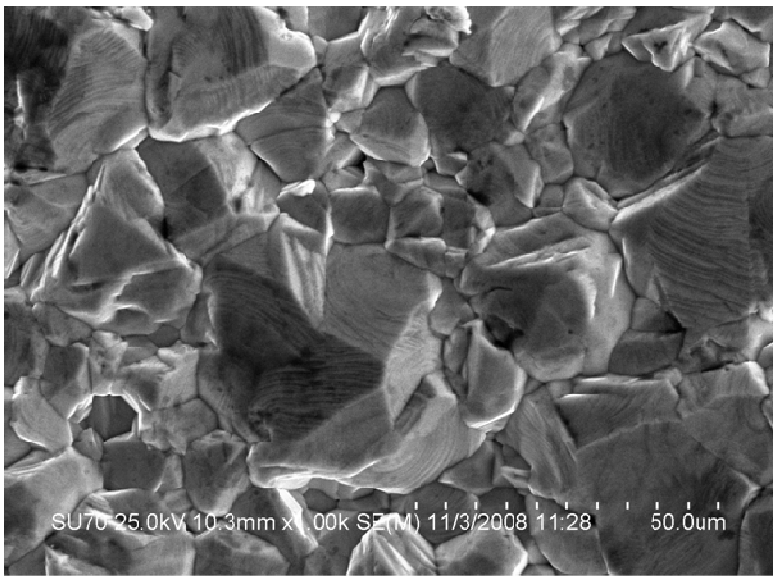
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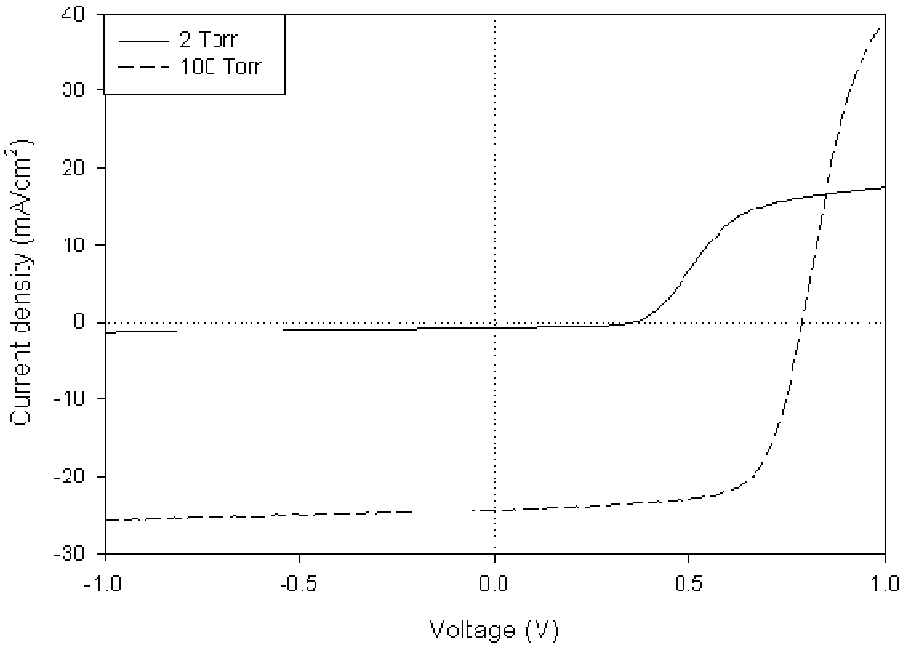
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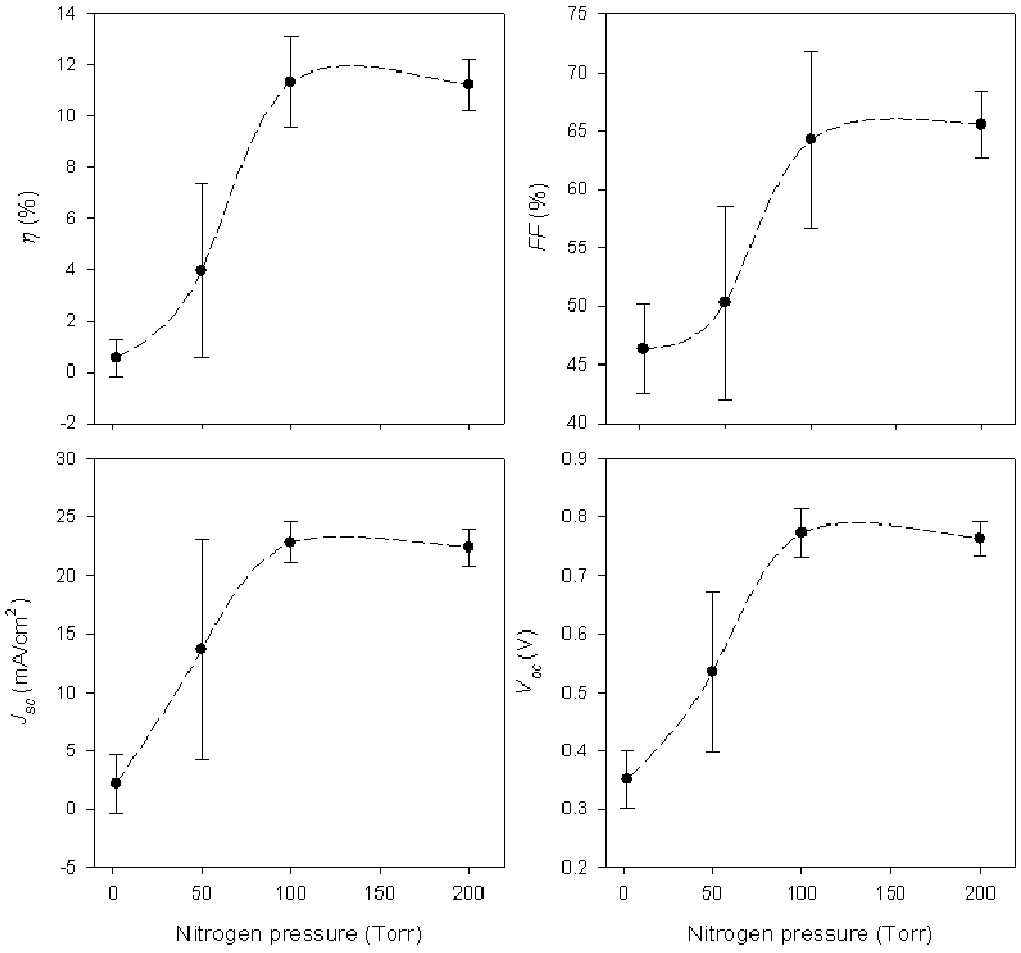
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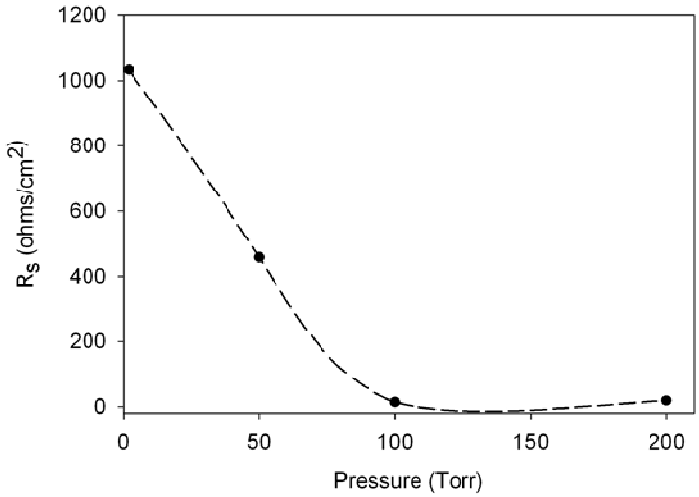
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